

EP 22385 (2)

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 753 867 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

15.01.1997 Bulletin 1997/03

(51) Int. Cl.⁶: H01F 1/057

(21) Application number: 96107388.9

(22) Date of filing: 09.05.1996

(84) Designated Contracting States:

DE FR GB

• Takahashi, Masahiro
Kumagaya-shi, Saitama-ken (JP)

(30) Priority: 12.07.1995 JP 175952/95

19.03.1996 JP 90400/96

• Taniguchi, Fumitake
Kumagaya-shi, Saitama-ken (JP)

(71) Applicant: HITACHI METALS, LTD.

Chiyoda-ku, Tokyo (JP)

(74) Representative: Beetz & Partner

Patentanwälte

Steinsdorfstrasse 10

80538 München (DE)

(72) Inventors:

• Uchida, Kimio

Kamisato-machi, Kodama-gun, Saitama-ken (JP)

(54) Rare earth permanent magnet and method for producing the same

(57) A rare earth permanent magnet consisting essentially, by weight, of 27.0-31.0 % of at least one rare earth element including Y, 0.5-2.0 % of B, 0.02-0.15 % of N, 0.25 % or less of O, 0.15 % or less of C, at least one optional element selected from the group consisting of 0.1-2.0 % of Nb, 0.02-2.0 % of Al, 0.3-5.0 % of Co, 0.01-0.5 % of Ga and 0.01-1.0 % of Cu, and a balance of Fe, and a production method thereof. The contents of rare earth element, oxygen, carbon and oxygen in the magnet are regulated within the specific ranges.

EP 0 753 867 A1

fine powder in a nitrogen containing atmosphere; (e) recovering the fine powder into a solvent in an inert gas atmosphere in the form of a slurry; (f) wet-compacting the slurry to form a green body while applying magnetic field; (g) heat-treating the green body in a vacuum furnace to remove the solvent therefrom; and (h) sintering the heat-treated green body in the vacuum furnace.

5 A fourth aspect of the present invention, there is provided a method for producing such rare earth permanent magnet, comprising the steps of (a) mixing a coarse powder of a first alloy mainly composed of $R_2Fe_{14}B$ phase, wherein R is at least one rare earth element including yttrium, and a coarse powder of a second alloy in a weight ratio of 70-99:1-30, the first alloy having a chemical composition, by weight, of 26.7-32 % of R, 0.9-2.0 % of B, 0.1-3.0 % of M wherein M is at least one of Ga, Al and Cu and balance Fe, and the second alloy having a chemical composition, by weight, of 10 35-70 % of R, 5-50 % of Co, 0.1-3.0 % of M and balance of Fe; (b) pulverizing the mixture of the coarse powders into a fine powder in a nitrogen containing atmosphere; (c) recovering the fine powder into a solvent in an inert gas atmosphere in the form of a slurry; (d) wet-compacting the slurry to form a green body while applying magnetic field; and (e) sintering the heat-treated green body in the vacuum furnace.

15 **BRIEF DESCRIPTION OF THE DRAWINGS**

Fig. 1 is a microphotograph showing the metal structure of a rare earth permanent magnet having a main phase in which the total area of crystal grains having a grain size of $10 \mu m$ or less is 96 % and the total area of crystal grains having a grain size of $13 \mu m$ or more is 1 %, each based on the total area of crystal grains in said main phase;

20 Fig. 2 is a microphotograph showing the metal structure of another rare earth permanent magnet having a main phase in which the total area of crystal grains having a grain size of $10 \mu m$ or less is 64 % and the total area of crystal grains having a grain size of $13 \mu m$ or more is 17 %, each based on the total area of crystal grains in said main phase;

25 Fig. 3 is a scanning electron microphotograph showing the cross sectional view of the rare earth permanent magnet shown in Fig. 1 after the passage of 5000 hours in corrosion test; and

Fig. 4 is a scanning electron microphotograph showing the cross sectional view of the rare earth permanent magnet shown in Fig. 2 after the passage of 2000 hours in corrosion test.

30 **DETAILED DESCRIPTION OF THE INVENTION**

First, the content of each element in the rare earth permanent magnet of the present invention will be described below.

The rare earth element referred to in the present invention is at least one element selected from the group consisting of lanthanides and yttrium. The content of the rare earth element is 27.0-31.0 weight % based on the total weight of the rare earth permanent magnet. When the content exceeds 31.0 weight %, the amount and the size of the R-rich phase in the sintered magnet become unfavorably larger to reduce the corrosion resistance. On the other hand, when the content is less than 27.0 weight %, a dense sintered magnet is not obtained because insufficient amount of the liquid phase, which is required for densification, during sintering operation. As a result thereof, the magnetic properties, in particular the residual magnetic flux density (Br) and coercive force (iHc), are decreased.

40 A preferred rare earth element may include Nd, Pr and Dy. Pr may be preferably contained in the rare earth permanent magnet in an amount of 0.1-10 weight %, and Dy in an amount of 0.5-15 weight %. Since Dy improves coercive force (iHc), it is further preferable for Dy to be contained in an amount of 0.8-10 weight %.

The content of oxygen is 0.05-0.25 weight %, preferably 0.2 weight % or less based on the total weight of the rare earth permanent magnet. When the content is larger than 0.25 weight %, since a part of the rare earth element is converted to oxides to reduce the amount of the rare earth element which directly contributes to the magnetic properties of magnet, the coercive force (iHc) is lowered. Since an alloy ingot from which an alloy powder to be sintered is produced inevitably contains 0.04 weight % of oxygen, the oxygen content in the final sintered magnet is practically difficult to be reduced to a level lower than 0.05 weight %.

50 The content of carbon is 0.01-0.15 weight %, 0.12 weight % or less, more preferably 0.10 weight % or less based on the total weight of the rare earth permanent magnet. When the content is higher than 0.15 weight %, since a part of the rare earth element is consumed to form carbides to reduce the amount of the rare earth element which directly contributes to the magnetic properties of magnet, the coercive force (iHc) is lowered. Since an alloy ingot from which an alloy powder to be sintered is produced inevitably contains 0.008 weight % of carbon, the carbon content in the final sintered magnet is practically difficult to be reduced to a level lower than 0.01 weight %.

55 From the inventor's studies, it has been found that the content of nitrogen should be strictly controlled in addition to regulating the content of rare earth element within 27.0-31.0 weight % to improve the corrosion resistance of the R-Fe-B-based, sintered permanent magnet. An excellent corrosion resistance and high magnetic properties can be simultaneously attained by controlling the nitrogen content to 0.02-0.15 weight %, preferably 0.03-0.13 weight % based on the total weight of the R-Fe-B-based, sintered permanent magnet along with controlling the contents of the rare earth ele-

stand in air under the condition of 2 atm., 120°C and 100% relative humidity to observe the degree of exfoliation of the Ni-plating that occurred with the passage of time. In the rare earth permanent magnet having a uniformly fine grain structure as shown in Fig. 1, no abnormality or change was observed in the Ni-plating even after the passage of 2500 hours. On the other hand, in the rare earth permanent magnet having a coarser grain size as shown in Fig. 2, a significant exfoliation of the Ni-plating was observed after the passage of 2000 hours although no exfoliation after the passage of 1000 hours. Since the above corrosion test was conducted in accelerated manner, both the rare earth permanent magnets may be put into practical use without any problems in their corrosion resistance. However, the results of the above test clearly demonstrate that the corrosion resistance is further improved by the uniform and fine grain structure as defined above.

Fig. 3 is a scanning electron microphotograph showing the cross sectional view of the rare earth permanent magnet shown in Fig. 1 after the passage of 5000 hours of the corrosion test. Fig. 4 is a scanning electron microphotograph showing the cross sectional view of the rare earth permanent magnet shown in Fig. 2 after the passage of 2000 hours of the corrosion test. In Fig. 3, although a slight exfoliation of the Ni-plating from the substrate (permanent magnet) occurs partially, the bonding between the Ni-plating and the substrate is good in view of practical use. Further, it can be seen that the metal structure of the rare earth permanent magnet is scarcely fractured by the corrosion test. In Fig. 4 having a coarse grain structure, it can be seen that a large exfoliation of the Ni-plating occurs due to the intergranular fracture in the metal structure of the substrate. From the results above, it has been found that the intergranular fracture by the accelerated corrosion test largely depends on the size of the grains in the main phase of permanent magnet.

The intergranular fracture of coarse grain structure is presumed to occur as follows. In the main phase having a relatively coarse grain structure as shown in Fig. 2, the intergranular space, mainly a grain boundary triple point, is occupied with an increased amount of the Nd-rich phase which is extremely susceptible to be oxidized. The factor responsible for corrosion fracture, for example, moisture in the above accelerated corrosion test, penetrates into the magnet intergranularly to cause the oxidation of the Nd-rich phase. Such oxidation of the Nd-rich phase may be considered to cause the chain intergranular fracture.

As described above, the corrosion resistance of the R-Fe-B-based, sintered permanent magnet can be further improved by the uniform and fine grain structure of the main phase defined as a main phase in which the total area of crystal grains of a grain size of 10 μm or less is 80 % or more and the total area of crystal grains of a grain size of 13 μm or more is 10 % or less, each based on the total area of crystal grains in said main phase.

The R-Fe-B-based, sintered permanent magnet of the present invention may be produced by the method described below.

Although the R-Fe-B-based starting coarse powder may be obtained by pulverizing an alloy ingot, a coarse powder obtained by pulverizing an alloy strip produced by a strip-casting method is preferable. The "strip-casting method" referred to in the present invention is a production method of alloy strip by injecting an alloy melt onto the surface of a cooling roll, etc. to quench the melt alloy, thereby forming alloy strip on the surface. It is important for obtaining a rare earth permanent magnet having a fine and uniform metal structure to sinter a fine powder having a uniform metal structure and a narrow particle size distribution. To obtain such a fine powder having an average particle size of 1-8 μm , preferably 3-5 μm , it is preferred to heat-treat an alloy ingot or an alloy strip, coarsely pulverize the heat-treated alloy ingot or alloy strip to coarse powder, and then finely pulverize the coarse powder in a nitrogen containing atmosphere.

Since an R-Fe-B-based alloy ingot usually includes in the alloy structure a precipitated α -Fe phase, the alloy ingot should be subjected to solution heat-treatment; prior to being pulverized; at 1000 - 1200°C for 1-10 hours in an inert gas atmosphere or in vacuo to dissipate the α -Fe phase.

An alloy strip produced by rapidly quenching an alloy melt on a cooling surface in accordance with the strip-casting method has a fine metal structure. However, a fine powder having a narrow particle size distribution is not obtained by simply pulverizing the alloy strip due to the hard surface of the alloy strip which is formed during the strip-casting by rapid quenching of molten metal on a cooling roll. The inventors have found that the alloy strip can be pulverized to a fine powder having a narrow particle size distribution when subjected to heat treatment at 800-1100°C, preferably 950-1050°C for 10 minutes to 10 hours in an inert gas atmosphere or in vacuum prior to being pulverized.

Although a mechanical pulverization may be employed in the present invention, the coarse pulverization is preferred to be carried out by spontaneously degrading the heat-treated alloy ingot or alloy strip by hydrogen occlusion thereto, and dehydrogenating. The hydrogen occlusion is carried out by keeping the alloy strips in a furnace filled with hydrogen gas under a pressure of 1 atm. or less at normal temperature for until the alloy strips is sufficiently degraded. The occluded hydrogen embrittles the R-rich phase of the alloy strip to make the alloy strip easily degraded to a coarse powder of a narrow particle size distribution. Then, the furnace is evacuated and heated to 150-550 °C, and the degraded strips are held there for 30 minutes to 10 hours to complete the dehydrogenation. After the coarse pulverization by hydrogen-occlusion, the coarse powder may be further coarsely pulverized mechanically in the known manner. The coarse powder thus obtained preferably has a particle size of 32 mesh or less.

The starting coarse powder is obtained as described above. Further, the starting coarse powder may be a mixture of a coarse powder of first alloy and a coarse powder of second alloy, both the coarse powder being produced by heat-treating an alloy strip obtained by a strip-casting method and coarsely pulverizing the heat-treated alloy strip by hydro-

Then, the coarse powder was finely pulverized under a pressure of 73.545 N/cm^2 (7.5 kgf/cm 2) while feeding the coarse powder into the jet mill at a rate of 8 kg/h.

After completion of fine pulverization, the fine powder was recovered from the jet mill directly into a mineral oil (Idemitsu Super Sol PA-30, trade name, manufactured by Idemitsu Kosan Co., Ltd.) in the Ar gas atmosphere. The recovered fine powder was made into a slurry having a solid content of 75 weight % by adjusting the amount of the mineral oil. The average particle size of the fine powder was 4.7 μm .

The slurry was then subjected to wet-compacting in a mold cavity while applying an orientation magnetic field of 1114.4 kA/m (14 kOe) and a molding pressure of 1.0 ton/cm 2 . The orientation magnetic field and the molding pressure were applied in the directions perpendicular to each other to form a green body. During the wet-compacting, a portion of mineral oil was discharged from a plurality of holes of the upper punch equipped with the mold cavity through a cloth filter of 1 mm thick.

The green body thus formed was heated in a vacuum furnace at 200 $^{\circ}\text{C}$ for one hour under a vacuum degree of 4 Pa (3.0×10^{-2} Torr) to remove the residual mineral oil. Then the temperature of the vacuum furnace was raised at a rate of 15 $^{\circ}\text{C}/\text{min}$ to 1070 $^{\circ}\text{C}$ under a vacuum degree of 0.0533 Pa (4.0×10^{-4} Torr). The temperature was maintained at 1070 $^{\circ}\text{C}$ for 3 hours to complete the sintering of the green body, thereby obtaining a rare earth permanent magnet.

The rare earth permanent magnet was found to have a composition as shown in Table 1. The rare earth permanent magnet was further subjected to heat-treatment at 900 $^{\circ}\text{C}$ for 2 hours and at 530 $^{\circ}\text{C}$ for 1 hour, each in Ar gas atmosphere. Upon measuring the magnetic properties (residual magnetic flux density: Br; coercive force: iHc; and maximum energy product: (BH)max) after machining, the rare earth permanent magnet was found to have good magnetic properties as shown in Table 1.

To evaluate the corrosion resistance of the rare earth permanent magnet, the surface of a test sample of 8 mm x 8 mm x 2 mm obtained by machining the rare earth permanent magnet was plated with Ni into 10 μm thick. The Ni-plated test sample was allowed to stand in air under the conditions of 2 atm., 120 $^{\circ}\text{C}$ and 100% of relative humidity. The degree of exfoliation of the Ni-plating from the surface of the rare earth permanent magnet was observed. As shown in Table 1, the rare earth permanent magnet exhibited a good corrosion resistance because no change was observed in the Ni-plating even after the passage of 1000 hours.

Example 2

The same starting coarse powder as used in Example 1 was finely pulverized in the same manner as in Example 1 except for adjusting the nitrogen content in the Ar gas atmosphere to 0.006 vol. % to obtain a slurry containing a fine powder having an average particle size of 4.8 μm . The slurry was further subjected to the same procedure as in Example 1 to obtain a rare earth permanent magnet having a composition shown in Table 1.

The magnetic properties and the result of the same corrosion test as in Example 1 are shown in Table 1. As seen from Table 1, the rare earth permanent magnet had good magnetic properties and no change in the Ni-plating was observed even after the passage of 1200 hours.

Example 3

The same starting coarse powder as used in Example 1 was finely pulverized in the same manner as in Example 1 except for adjusting the nitrogen content in the Ar gas atmosphere to 0.015 vol. % to obtain a slurry containing a fine powder having an average particle size of 4.7 μm . The slurry was further subjected to the same procedure as in Example 1 to obtain a rare earth permanent magnet having a composition shown in Table 1.

The magnetic properties and the result of the same corrosion test as in Example 1 are shown in Table 1. As seen from Table 1, the rare earth permanent magnet had good magnetic properties and no change in the Ni-plating was observed even after the passage of 1500 hours.

Comparative Example 1

The same starting coarse powder as used in Example 1 was finely pulverized in the same manner as in Example 1 except for adjusting the nitrogen content in the Ar gas atmosphere to 0.00005 vol. % to obtain a slurry containing a fine powder having an average particle size of 4.7 μm . The slurry was further subjected to the same procedure as in Example 1 to obtain a rare earth permanent magnet having a composition shown in Table 1.

The magnetic properties and the result of the same corrosion test as in Example 1 are shown in Table 1. As seen from Table 1, although the rare earth permanent magnet had good magnetic properties, the corrosion resistance was extremely poor because the Ni-plating began to exfoliate after the passage of 120 hours.

from Table 1, the rare earth permanent magnet showed a good corrosion resistance because no change in the Ni-plating was observed even after the passage of 1200 hours. However, the rare earth permanent magnet has poor magnetic properties, in particular, the coercive force (iHc) was too low to be put into practice.

5

Table 1 (to be contd.)

Chemical Composition of Magnet (weight %)														
No.	Nd	Pr	Dy	B	Fe	Nb	Al	Co	Ga	Cu	N	O	C	
<u>Examples</u>														
10	1	23.9	2.9	2.0	1.1	bal.	1.2	1.0	3.3	0.1	-	0.03	0.17	0.06
	2	23.9	2.9	2.0	1.1	bal.	1.2	1.0	3.3	0.1	-	0.05	0.16	0.06
	3	23.9	2.9	2.0	1.1	bal.	1.2	1.0	3.3	0.1	-	0.12	0.16	0.06
15	<u>Comparative Examples</u>													
	1	23.9	2.9	2.0	1.1	bal.	1.2	1.0	3.3	0.1	-	0.01	0.18	0.06
	2	23.9	2.9	2.0	1.1	bal.	1.2	1.0	3.3	0.1	-	0.20	0.18	0.06
20	3	26.7	3.5	2.0	1.1	bal.	1.3	1.0	3.3	0.1	-	0.04	0.20	0.07
	4	23.9	2.9	2.0	1.1	bal.	1.2	1.0	3.3	0.1	-	0.05	0.30	0.06
	5	23.9	2.9	2.0	1.1	bal.	1.2	1.0	3.3	0.1	-	0.06	0.16	0.18
25	6	23.9	2.9	2.0	1.1	bal.	1.2	1.0	3.3	0.1	-	0.05	0.29	0.17

Table 1 (contd.)

No.	Br (kG)	Magnetic Properties		Corrosion Resistance
		iHc (kOe)	(BH)max (MGOe)	
<u>Examples</u>				
30	1	13.7	14.5	45.5 No change in Ni-plating after 1000 hrs.
35	2	13.7	14.4	45.5 No change in Ni-plating after 1200 hrs.
	3	13.7	14.2	45.5 No change in Ni-plating after 1500 hrs.
<u>Comparative Examples</u>				
40	1	13.7	14.6	45.5 Exfoliation of Ni-plating after 120 hrs.
	2	13.7	11.0	44.8 No change in Ni-plating after 1800 hrs.
	3	13.0	17.0	40.5 Exfoliation of Ni-plating after 24 hrs.
45	4	13.7	10.5	44.1 No change in Ni-plating after 1200 hrs.
	5	13.7	10.8	44.3 No change in Ni-plating after 1200 hrs.
	6	13.7	7.5	42.5 No change in Ni-plating after 1200 hrs.

* 10 kG = 1 T ** 1 kOe = 79.6 kA/m

50

Example 4

55

An alloy strips of 0.2-0.5 mm thick having a chemical composition, by weight, of 27.0% of Nd, 0.5% of Pr, 1.5% of Dy, 1.05% of B, 0.35% of Nb, 0.08% of Al, 2.5% of Co, 0.09% of Ga, 0.08% of Cu, 0.03% of O, 0.005% of C, 0.004% of N and balance of Fe were produced by a strip-casting method. After being heat-treated at 1000°C for 2 hours in Ar gas atmosphere, the alloy strips were spontaneously degraded by hydrogen occlusion in a furnace at room temperature.

filter of 1 mm thick.

The green body thus formed was heated in a vacuum furnace at 200 °C for 2 hours under a vacuum degree of 6.67 Pa (5.0×10^{-2} Torr) to remove the residual mineral oil. Then, the temperature of the vacuum furnace was raised at a rate of 15 °C/min to 1090 °C under a vacuum degree of 0.0667 Pa (5.0×10^{-4} Torr). The temperature was maintained at 1090 °C for 3 hours to complete the sintering of the green body, thereby obtaining a rare earth permanent magnet having a chemical composition as shown in Table 2.

The area ratios of grains in the main phase of the rare earth permanent magnet obtained in the same manner as in Example 4 are shown in Table 2.

The rare earth permanent magnet was further subjected to heat-treatment at 900°C for 2 hours and at 460°C for 1 hour, each in Ar gas atmosphere.

The magnetic properties and the result of the same corrosion test as in Example 1 are shown in Table 2. As seen from Table 2, the rare earth permanent magnet had good magnetic properties and no change in the Ni-plating was observed even after the passage of 2500 hours.

15 **Example 6**

An alloy strips of 0.1-0.5 mm thick having a chemical composition, by weight, of 20.7% of Nd, 8.6% of Pr, 1.2% of Dy, 1.05% of B, 0.08% of Al, 2.0% of Co, 0.09% of Ga, 0.1% of Cu, 0.03% of O, 0.006% of C, 0.004% of N and balance of Fe were produced by a strip-casting method. After being heat-treated at 900°C for 3 hours in Ar gas atmosphere, the 20 alloy strips were subjected to the same hydrogen-occlusion, dehydrogenation and mechanical pulverization as in Example 4 to obtain a starting coarse powder of 32 mesh or less having a chemical composition, by weight, of 20.7% of Nd, 8.6% of Pr, 1.5% of Dy, 1.05% of B, 0.08% of Al, 2.0% of Co, 0.09% of Ga, 0.1% of Cu, 0.13% of O, 0.03% of C, 0.009% of N and balance of Fe.

After 50 kg of the starting coarse powder was introduced into a jet mill, the inner atmosphere of the jet mill was 25 replaced with Ar gas while controlling the oxygen content in the Ar gas atmosphere to substantially zero % (0.002 vol. % under an oxygen analyzer). The nitrogen content in the Ar gas atmosphere was adjusted to 0.005 vol. % by introducing N₂ gas into the Ar gas atmosphere. Then, the coarse powder was finely pulverized under a pressure of 73.5 N/cm² (7.5 kgf/cm²) while feeding the coarse powder into the jet mill at a rate of 8 kg/h.

After completion of fine pulverization, the fine powder was recovered from the jet mill directly into a mineral oil (Idemitsu Super Sol PA-30, trade name, manufactured by Idemitsu Kosan Co., Ltd.) in the Ar gas atmosphere. The recovered fine powder was made into a slurry having a solid content of 75 weight % by adjusting the amount of the mineral oil. The average particle size of the fine powder was 4.0 µm.

The slurry was then subjected to wet-compacting in a mold cavity while applying an orientation magnetic field of 1034.8 kA/m (13 kOe) and a molding pressure of 0.6 ton/cm². The orientation magnetic field and the molding pressure 35 were applied in the directions perpendicular to each other to form a green body. During the wet-compacting, a portion of mineral oil was discharged from a plurality of holes of the upper punch equipped with the mold cavity through a cloth filter of 1 mm thick.

The green body thus formed was heated in a vacuum furnace at 180 °C for 4 hours under a vacuum degree of 8 Pa (6.0×10^{-2} Torr) to remove the residual mineral oil. Then the temperature of the vacuum furnace was raised at a rate of 15 °C/min to 1070°C under a vacuum degree of 0.04 Pa (3.0×10^{-4} Torr). The temperature was maintained at 1070°C for 2 hours to complete the sintering of the green body, thereby obtaining a rare earth permanent magnet having a chemical composition as shown in Table 2.

The area ratios of grains in the main phase of the rare earth permanent magnet obtained in the same manner as in Example 4 are shown in Table 2.

45 The rare earth permanent magnet was further subjected to heat-treatment at 900°C for 2 hours and at 510°C for 1 hour, each in Ar gas atmosphere.

The magnetic properties and the result of the same corrosion test as in Example 1 are shown in Table 2. As seen from Table 2, the rare earth permanent magnet had good magnetic properties and no change in the Ni-plating was observed even after the passage of 2500 hours.

50

Example 7

An alloy strips of 0.1-0.4 mm thick having a chemical composition, by weight, of 22.0% of Nd, 5.0% of Pr, 1.5% of Dy, 1.1% of B, 1.0% of Al, 2.5% of Co, 0.02% of O, 0.005% of C, 0.005% of N and balance of Fe were produced by a 55 strip-casting method. After being heat-treated at 1000°C for 2 hours in Ar gas atmosphere, the alloy strips were coarsely pulverized mechanically in nitrogen gas atmosphere to obtain a starting coarse powder of 32 mesh or less having a chemical composition, by weight, of 22.0% of Nd, 5.0% of Pr, 1.5% of Dy, 1.1% of B, 1.1% of Al, 2.5% of Co, 0.1% of O, 0.01% of C, 0.009% of N and balance of Fe.

After 50 kg of the starting coarse powder was introduced into a jet mill, the inner atmosphere of the jet mill was

Comparative Example 7

5 In the same manner as in Example 6 except that N₂ gas was not introduced into the Ar gas atmosphere, a rare earth permanent magnet having a chemical composition as shown in Table 2 was produced. The average particle size of the fine powder was 4.0 µm.

The area ratios of grains in the main phase of the rare earth permanent magnet obtained in the same manner as in Example 4 are shown in Table 2.

Further, the magnetic properties and the result of the same corrosion test as in Example 1 are shown in Table 2. As seen from Table 2, although the rare earth permanent magnet had magnetic properties nearly equal to those of 10 Example 6, the corrosion resistance was extremely poor because the Ni-plating began to exfoliate only in 192 hours.

Comparative Example 8

15 An alloy strips of 0.2-0.5 mm thick having a chemical composition, by weight, of 30.0% of Nd, 0.5% of Pr, 1.5% of Dy, 1.05% of B, 0.8% of Nb, 0.2% of Al, 3.0% of Co, 0.08% of Ga, 0.1% of Cu, 0.02% of O, 0.005% of C, 0.005% of N and balance of Fe were produced by a strip-casting method. After being heat-treated at 950°C for 4 hours in Ar gas atmosphere, the alloy strips were subjected to the same hydrogen-occlusion, dehydrogenation and mechanical pulverization as in Example 4 to obtain a starting coarse powder of 32 mesh or less having a chemical composition, by weight, of 30.0% of Nd, 0.5% of Pr, 1.5% of Dy, 1.05% of B, 0.8% of Nb, 0.2% of Al, 3.0% of Co, 0.08% of Ga, 0.1% of Cu, 0.12% of O, 0.02% of C, 0.009% of N and balance of Fe.

20 After 100 kg of the starting coarse powder was introduced into a jet mill, the inner atmosphere of the jet mill was replaced with N₂ gas while controlling the oxygen content in the N₂ gas atmosphere to substantially zero % (0.001 vol. % under an oxygen analyzer). Then, the coarse powder was finely pulverized under a pressure of 73.545 N/cm² (7.5 kgf/cm²) while feeding the coarse powder into the jet mill at a rate of 10 kg/h.

25 After completion of fine pulverization, the fine powder was recovered from the jet mill directly into a mineral oil (Idemitsu Super Sol PA-30, trade name, manufactured by Idemitsu Kosan Co., Ltd.) in N₂ gas atmosphere. The recovered fine powder was made into a slurry having a solid content of 70 weight % by adjusting the amount of the mineral oil. The average particle size of the fine powder was 4.1 µm.

30 The slurry was then subjected to wet-compacting in a mold cavity while applying an orientation magnetic field of 1114.4 kA/m (14 kOe) and a molding pressure of 0.8 ton/cm². The orientation magnetic field and the molding pressure were applied in the directions perpendicular to each other to form a green body. During the wet-compacting, a portion of mineral oil was discharged from a plurality of holes of the upper punch equipped with the mold cavity through a cloth filter of 1 mm thick.

35 The green body thus formed was heated in a vacuum furnace at 180 °C for 2 hours under a vacuum degree of 6.67 (5.0 x 10⁻² Torr) to remove the residual mineral oil. Then the temperature of the vacuum furnace was raised at a rate of 15°C/min to 1080°C under a vacuum degree of 0.04 Pa (3.0 x 10⁻⁴ Torr). The temperature was maintained at 1080 °C for 3 hours to complete the sintering of the green body, thereby obtaining a rare earth permanent magnet having a chemical composition as shown in Table 2.

40 The area ratios of grains in the main phase of the rare earth permanent magnet obtained in the same manner as in Example 4 are shown in Table 2.

The rare earth permanent magnet was further subjected to heat-treatment at 900°C for 2 hours and at 550°C for 1 hour, each in Ar gas atmosphere.

45 The magnetic properties and the result of the same corrosion test as in Example 1 are shown in Table 2. As seen from Table 2, although the rare earth permanent magnet was good in magnetic properties, extremely poor in the corrosion resistance because the Ni-plating began to exfoliate only in 48 hours.

Separately, alloy B having a chemical composition shown in Table 3 was cast from the melt obtained by induction-heating in Ar gas atmosphere a mixture containing metal powders, each having a purity of 95% or higher, of Nd, Pr, Dy and Co.

5

Table 3

Alloy	Chemical Composition of Alloy											
	Nd	Pr	Dy	B	Nb	Co	Ga	Cu	O	N	C	Fe
A	27.5	0.45	-	1.17	-	-	0.09	0.11	0.010	0.004	0.005	bal.
B	31.5	0.50	15	-	-	20	-	-	0.012	0.006	0.003	bal.

15 Each of the alloy A and alloy B was occluded with hydrogen in an evacuated furnace, heated to 500°C while evacuating the furnace, cooled to room temperature, and coarsely pulverized to obtain a coarse powder of 32 mesh or less.

A starting powder blend containing 90 weight % of alloy A and 10 weight % of alloy B was prepared by uniformly mixing the coarse powders of alloys A and B in a V-type blender.

20 After the starting powder blend was introduced into a jet mill, the inner atmosphere of the jet mill was replaced with N₂ gas while controlling the oxygen content in the N₂ gas atmosphere to substantially zero % (0.001 vol. % under an oxygen analyzer). Then, the starting powder blend was finely pulverized under a pressure of 68.65 N/cm² (7.0 kgf/cm²) while feeding the powder blend into the jet mill at a rate of 10 kg/h.

25 After completion of fine pulverization, the fine powder gas recovered from the jet mill directly into a mineral oil (Idemitsu Super Sol PA-30, trade name, manufactured by Idemitsu Kosan Co., Ltd.) under N₂ gas atmosphere. The recovered fine powder was made into a slurry having a solid content of 78 weight % by adjusting the amount of the mineral oil. The average particle size of the fine powder was 4.5 µm.

30 The slurry was then subjected to wet-compacting in a mold cavity while applying an orientation magnetic field of 955.2 kA/m (12 kOe) and a molding pressure of 0.8 ton/cm². The orientation magnetic field and the molding pressure were applied in the directions perpendicular to each other to form a green body. During the wet-compacting, a portion of mineral oil was discharged from a plurality of holes of the upper punch equipped with the mold cavity through a cloth filter of 1 mm thick.

35 The green body thus formed was heated in a vacuum furnace at 200 °C for one hour under a vacuum degree of 6.67 Pa (5.0 x 10⁻² Torr) to remove the residual mineral oil. Then the temperature of the vacuum furnace was raised at a rate of 15°C/min to 1070°C under a vacuum degree of 0.00667 Pa (5 x 10⁻⁵ Torr). The temperature was maintained at 1070 °C for 2 hours to complete the sintering of the green body.

40 The sintered product was further subjected to heat-treatment at 900°C for 2 hours and at 500°C for 1 hour, each in Ar gas atmosphere to obtain a rare earth permanent magnet having a chemical composition as shown in Table 4.

The magnetic properties after machining and the corrosion resistance evaluated in the same manner as in Example 1 are shown in Table 5. As seen from Table 5, the rare earth permanent magnet had good magnetic properties.

45 From comparison of magnetic properties of Example 10 with those of Example 11 described below, it can be seen that the starting powder is preferred to be a powder blend of different alloys because the magnetic properties were further improved. Further, as seen from the result of corrosion test, the rare earth permanent magnet produced above showed a good corrosion resistance.

45 Comparative Example 9

The same powder blend (alloy A : alloy B = 90 : 10 by weight) as used in Example 10 was finely pulverized in the same manner as in Example 10 except that the fine powder was recovered from the jet mill into an empty container without using a solvent. In such a dry recovery, since the fine powder likely to ignite upon contacting with air when the oxygen content in the inner atmosphere of jet mill is too low, the fine pulverization was conducted while supplying oxygen gas to maintain the oxygen content in N₂ gas atmosphere to 0.1 vol. %. The average particle size of the dry fine powder thus prepared was 4.5 µm.

50 The dry fine powder was then subjected to dry-compacting in a mold cavity while applying an orientation magnetic field of 955.2 kA/m (12 kOe) and a molding pressure of 0.8 ton/cm². The orientation magnetic field and the molding pressure were applied in the directions perpendicular to each other.

55 The green body thus formed was sintered by kept at 1070°C for 2 hours under 0.00667 Pa (5.0 x 10⁻⁵ Torr), and then subjected to two-stage heat treatment in the same manner as in Example 10 to produce a rare earth permanent magnet having a chemical composition as shown in Table 4. The chemical composition of the rare earth permanent magnet thus produced was nearly equal to that of Example 10 except for the oxygen content (0.612%) and the carbon

10	blend	wet	14.1	16.3	47.5	7.60	No change after 2500 hrs.
11	single	wet	13.9	15.0	46.0	7.58	No change after 2500 hrs.
Comparative Example							
9	blend	dry	13.5	11.5	43.3	7.42	No change after 2500 hrs.

10

Example 12

15 In the same manner as in Example 10, a slurry containing a fine powder having an average particle size of 4.1 μm was prepared from a starting powder blend consisting of 85 weight % of alloy C and 15 weight % of alloy D, each having a chemical composition shown in Table 6.

20

Table 6

Alloy	Chemical Composition of Alloy											
	Nd	Pr	Dy	B	Nb	Co	Ga	Cu	O	N	C	Fe
C	27.0	0.40	-	1.18	-	-	0.10	0.12	0.011	0.004	0.004	bal.
D	5.5	0.50	40	-	-	20	-	-	0.013	0.006	0.003	bal.

30 The slurry was wet-compacted in the same as in Example 10 to form a green body. After heated in a vacuum furnace at 200°C for one hour under a vacuum degree of 6.67 Pa (5.0×10^{-2} Torr) to remove the residual mineral oil, the green body was heated to 1080°C at a rate of 15°C/min and sintered at 1080°C for 2 hours under a vacuum degree of 0.00667 Pa (5.0×10^{-5} Torr). The sintered product was further subjected to heat-treatment at 900°C for 2 hours and at 480°C for 1 hour, each in Ar gas atmosphere to obtain a rare earth permanent magnet having a chemical composition as shown in Table 7.

35 The magnetic properties after machining and the corrosion resistance evaluated in the same manner as in Example 1 are shown in Table 8. As seen from Table 8, the rare earth permanent magnet had good magnetic properties. From comparison of magnetic properties of Example 12 with those of Example 13 described below, it can be seen that the starting powder is preferred to be a powder blend of different alloys because the magnetic properties were further improved. Further, as seen from the result of corrosion test, the rare earth permanent magnet produced above showed a good corrosion resistance.

Comparative Example 10

40 The same powder blend as used in Example 12 was treated in the same manner as in Comparative Example 9 to obtain a fine powder having an average particle size of 4.1 μm . The fine powder was dry-compacted and sintered in the same manner as in Comparative Example 9 except for sintered at 1080°C. The sintered product was subjected to the same heat treatment as in Example 12 to produce a rare earth permanent magnet having a chemical composition shown in Table 7, which chemical composition was nearly equal to that of Example 12 except for the oxygen content and the carbon content.

45 The magnetic properties after machining and the corrosion resistance evaluated in the same manner as in Example 1 are shown in Table 8. From the same reason as mentioned in Comparative Example 9, the rare earth permanent magnet was quite inferior in magnetic properties (Br , iHc and $(\text{BH})_{\text{max}}$) as compared with Example 12.

Example 13

55

A rare earth permanent magnet having nearly the same chemical composition as that of Example 12 was produced from a starting powder of single alloy as follows.

A mixture of metal powders, each having a purity of 95% or higher, of Nd, Pr, Dy, B, Co, Ga, Cu and Fe were strip-cast under the same conditions as in Example 12 to prepare alloy strips having a chemical composition, by weight, of

substantially 0 % of oxygen or in argon gas atmosphere containing substantially 0 % of oxygen and 0.0001-0.1 volume-% of nitrogen under a pressure of 49-98.1 N/cm² (5-10 kgf/cm²) while feeding said coarse powder into said mill at a feeding rate of 3-20 kg/h;

5 recovering the fine powder into a solvent in nitrogen gas atmosphere or argon gas atmosphere in the form of a slurry;

wet-compacting said slurry to form a green body while applying magnetic field;

heat-treating said green body in a vacuum furnace to remove said solvent therefrom; and
sintering said heat-treated green body in said vacuum furnace.

10 5. The method according to claim 4, wherein said coarse powder is obtained by

strip-casting a melt of said R-Fe-B-based alloy into an alloy strip having 1 mm thickness or less;
heat-treating said alloy strip at 800-1100 °C in an inert gas atmosphere or in vacuo; and
coarsely pulverizing said heat-treated alloy strip.

15 6. A method for producing a rare earth permanent magnet according to anyone of claims 1-3, comprising the steps of:

strip-casting a melt of an R-Fe-B-based alloy having a composition corresponding to the composition recited in claim 1, except for the N, O and C contents, into an alloy strip having 1 mm thickness or less;

20 heat-treating said alloy strip at 800-1100°C in an inert gas atmosphere or in vacuo;

pulverizing said heat-treated alloy strip into a coarse powder;

pulverizing said coarse powder into a fine powder in a nitrogen containing atmosphere,

recovering the fine powder into a solvent in an inert gas atmosphere in the form of a slurry;

wet-compacting said slurry to form a green body while applying magnetic field;

heat-treating said green body in a vacuum furnace to remove said solvent therefrom; and

25 sintering said heat-treated green body in said vacuum furnace.

7. The method according to claim 6, wherein said coarse powder is finely pulverized in nitrogen gas atmosphere containing substantially 0 % of oxygen or in argon gas atmosphere containing substantially 0 % of oxygen and 0.0001-0.1 volume-% of nitrogen under a pressure of 49-98.1 N/cm² (5-10 kgf/cm²) while feeding said coarse powder into said mill at a feeding rate of 3-20 kg/h.

30 8. A method for producing a rare earth permanent magnet according to anyone of claims 1-3, comprising the steps of:

35 mixing a coarse powder of a first alloy mainly composed of $R_2Fe_{14}B$ phase, wherein R is at least one rare earth element including yttrium, and a coarse powder of a second alloy in a weight ratio of 70-99:1-30, said first alloy having a chemical composition, by weight, of 26.7-31 % of R, 0.9-2.0 % of B, 0.1-3.0 % of M wherein M is at least one of Ga, Al and Cu and balance of Fe, and said second alloy having a chemical composition, by weight, of 35-70 % of R, 5-50 % of Co, 0.1-3.0 % of M and balance of Fe;

40 pulverizing the mixture of said coarse powders into a fine powder in a nitrogen containing atmosphere;

recovering the fine powder into a solvent in an inert gas atmosphere in the form of a slurry;

wet-compacting said slurry to form a green body while applying magnetic field; and

sintering said heat-treated green body in said vacuum furnace.

45 9. The method according to claim 8, wherein said coarse powder of first alloy is obtained by

strip-casting a melt of said first alloy into an alloy strip having 1 mm thickness or less;

heat-treating said alloy strip at 800-1100 °C in an inert gas atmosphere or in vacuo; and

coarsely pulverizing said heat-treated alloy strip.

50 10. The method according to any one of claims 5 to 9, wherein said coarse pulverization of said heat-treated alloy strips is carried out by spontaneously degrading said alloy by hydrogen occlusion and subsequently dehydrogenating said degraded alloy.

55 11. The method according to any one of claims 4 to 10, wherein said slurry is wet-compacted by compression molding.

12. The method according to any one of claims 4 to 11, wherein said solvent for said slurry is selected from the group consisting of mineral oils, synthetic oils and vegetable oils, each having a flash point of 70 °C or higher and less than 200 °C under 1 atm, a fractionating point of 400 °C or less and a kinematic viscosity of 10 mm²/s (10 cSt) or

FIG. 1

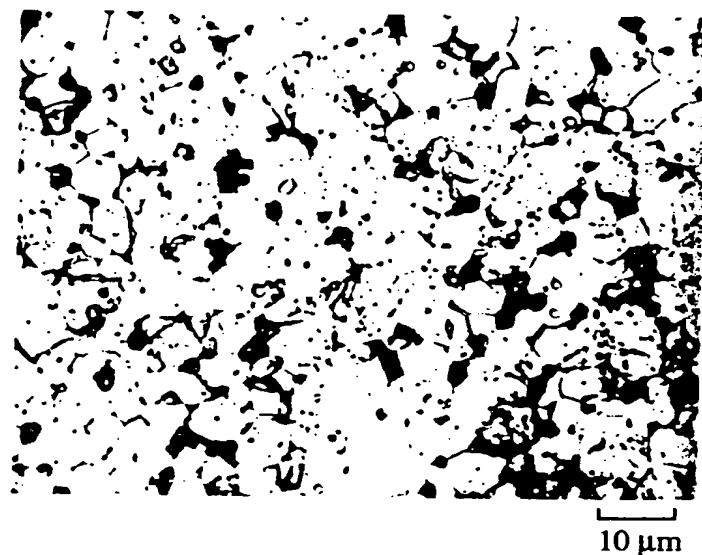
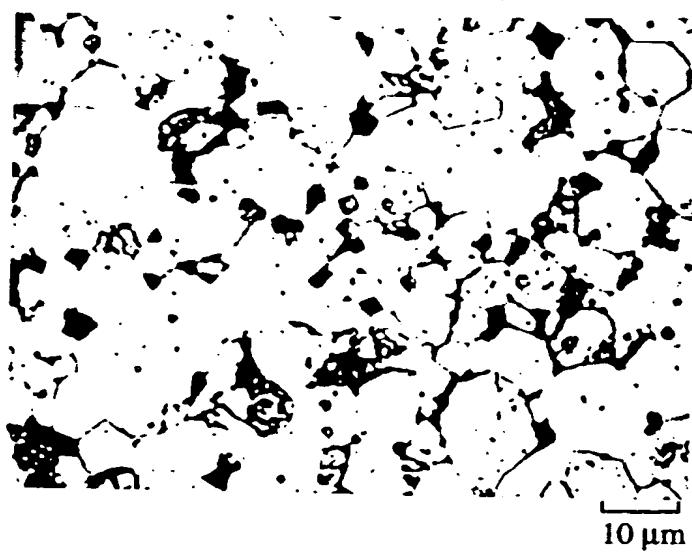


FIG. 2





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 10 7388

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.6)						
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim							
X	PATENT ABSTRACTS OF JAPAN vol. 012, no. 028 (C-471), 27 January 1988 & JP-A-62 177147 (DAIDO STEEL CO LTD), 4 August 1987, * abstract *	1	H01F1/057						
A	EP-A-0 633 581 (SUMITOMO SPEC METALS) 11 January 1995 * page 8, line 11 - line 43 * * page 10, line 45 - line 47; example 1 *	1-5,10							
A	PATENT ABSTRACTS OF JAPAN vol. 016, no. 347 (E-1240), 27 July 1992 & JP-A-04 107903 (SUMITOMO METAL MINING CO LTD), 9 April 1992, * abstract *	1,3,4							
A	PATENT ABSTRACTS OF JAPAN vol. 94, no. 011 & JP-A-06 322469 (HITACHI METALS LTD), 22 November 1994, * abstract *	1,4,8, 11,12							
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)						
			H01F						
<p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 34%;">Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>7 October 1996</td> <td>Decanniere, L</td> </tr> </table>				Place of search	Date of completion of the search	Examiner	THE HAGUE	7 October 1996	Decanniere, L
Place of search	Date of completion of the search	Examiner							
THE HAGUE	7 October 1996	Decanniere, L							
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document							
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document									